Technique For Measuring Swelling Tendency and Coke Density For Catalytic Coal Gasification

Claude C. Culross, LeRoy R. Clavenna and Richard D. Williams

Exxon Research and Engineering Company
P. O. Box 4255
Baytown, Texas 77522

Introduction

Since 1979, Exxon Research and Engineering Company has operated a one ton-per-day Process Development Unit (PDU) at Baytown, Texas in support of the development of the Catalytic Coal Gasification Process (CCG). Details of this process development effort are available elsewhere[1a-c]. This paper summarizes responses of coal, particularly swelling and coke density, to gasification conditions; some characteristics of the five coals which have been processed in the PDU are given in Table 1. The PDU utilizes a high pressure fluidized bed gasifier that operates at 3.4 MPa (500 psia) and 978°K (1300°F). Coal is typically catalyzed by wet mixing with potassium salts (KOH, K_2CO_3) prior to introduction into the gasifier. The alkali catalyst promotes gasification, shift, and methanation in a single thermoneutral reactor. Another important catalyst benefit is that it reduces the thermoplasticity of bituminous coals at the same time; however, enough thermoplasticity persists that its impact must be considered when operating a fluid bed gasifier (Figure 1). The thermoplasticity manifests itself as agglomeration which occurs during the transient plastic state and as swollen, structurally weak particles.

Because CCG conditions, viz., high heat-up rate and high pressure, are quite different from the conditions at which conventional tests for thermoplasticity are carried out, it seemed important to develop a technique which best reproduced the CCG conditions. This view is well supported in the literature. In the pyrolysis of coal, both an increase of heating rate[2a-d] and pressure [2b,c,e,f] have been associated with decreased viscosity or increased fluidity during the plastic transition of coal. The reduced viscosity associated with increased heating rate is normally attributed to the rapidly increasing temperature which occurs during pyrolysis. This rapid temperature increase results in an enrichment of the liquid products in the plastic mass at a higher temperature. The effect of increased pressure is to repress evolution of the low viscosity, volatile components from the plastic coal.

Typically, swelling is increased by factors that decrease viscosity during the plastic transition. There is general agreement in the literature that an increased heating rate increases the potential for greater swelling[2a,b]. However, the influence of pressure on swelling is not as clear. Increased pressure reduces viscosity but also, because of compression, reduces the total volume of gases that are released and available to swell the plastic coal. Increasing the pressure has been reported to increase[2b,f], decrease[2g], or have little effect[2c,h] on swelling. The differences are likely due to the different procedures and physical arrangement of the techniques used to measure swelling. Therefore, it was important for us to choose a technique for measuring swelling that was applicable to our high pressure fluid bed in that it would be capable of differentiating good performance potential in a feed coal from marginal or unacceptable potential. In addition, the technique had to be simple and relatively fast for use as a quality control test.

This paper outlines the technique developed and illustrates the use of the test in the study of the impact of process variables of interest (catalyst, catalyst distribution, coal pretreatment, pressure, gas atmosphere) on coal thermoplasticity.

Free Fall Swelling Test

A simple, easy to use laboratory test unit was devised to study coal thermoplasticity within the context of CCG conditions. The test, known as the Free Fall Swelling Test, simulates major CCG process variables such as high pressure and high heat-up rate. A schematic of the Free Fall Unit is shown in Figure 2.

Pressure is controlled by a back pressure regulator 8 (typically between 0.1 and 3.5 MPa). Coal aliquots (150µm x 600µm, 0.25 g ± 0.01g) are fed through a set of two valves to the hot drop tube via the feedline 3. The coal particles fall freely through the heated zone (typically operated in the temperature range of 978-1033°K) where they are rapidly heated, pyrolyzed, and form coke or char. A particle heat-up model was applied to estimate heat-up rates and free fall residence times. Time average heat-up rates range from 2,800 to 11,000°K/sec for the range of particle sizes used. The solid residue is removed from the drop tube by withdrawing the quartz liner. The use of a quartz liner allows easy and complete removal of the residue and gives visible evidence that tar evolution has ceased before the residue reaches the bottom of the liner.

On cooling, a measure is made of residue loose bulk density (equation 1) and swelling (equation 2). Generally speaking, residue densities are less than coal densities because of the combined effect of mass loss and swelling due to the transient thermoplastic state, and the densities usually vary between 0.05 and 0.55 g/cc. The Free Fall Swelling Index (FFSI, equation 2) is a measure of swelling, and it usually varies between 1.0 (no swelling) and 12.0 (a twelve-fold increase in loose bulk volume relative to the starting coal).

$$\text{Residue Loose Bulk Density} = \frac{\text{Residue Mass (g)}}{\text{Loose Bulk Volume (cc)}} \qquad (1)$$

$$\text{Free Fall Swelling Index} = \text{FFSI} = \frac{\text{Residue Loose Bulk Volume (cc)}}{\text{Coal Loose Bulk Volume (cc)}} \qquad (2)$$

The need to develop an alternative to conventional tests for thermoplastic tendency is made more clear by the data in Table 2, a comparison of ASTM Free Swelling Index (FSI) and the FFSI of selected coals determined under CCG conditions. The ASTM FSI's are all low, that is, there is no swelling and little or no agglomeration, but the FFSI's range from 1.0 to 5.6. There are also clear morphological differences in the residues from both tests. The FSI residues are granular solids which retain the sharp edges and dull surfaces found in the original coal. But the free fall residues "B" and "C" are composed of bloated, reflective spheres which appear to have gone through a fluid stage (as in Figure 1). The thermoplasticity implied by the morphological differences between coal and pyrolyzed residue was later directly observed by capturing on film the behavior of rapidly heated single particles of catalyzed Illinois No. 6 coal in a fast photography cell (FILM SEGMENT #1: Illinois + 12.2 wt % KOH, 0.1 MPa helium, filament heat-up rate = 1000°K/sec). Melting, bubbling, swelling, and thermosetting were clearly evident.

The possibility that a coal could exhibit no swelling at low heat-up rate but exhibit distinct swelling at a higher heat-up rate is implied by the work of Van Krevelen[2a]. Therefore, the contrasting FSI and FFSI results obtained here come as no surprise because of the large difference in heat-up rates (FSI = 5°K/sec, FFSI >1000°K/sec). Since the conditions of the Free Fall Swelling Test more nearly resemble CCG conditions, and because swelling behavior in the test is at least qualitatively more in line with behavior in a fluid bed gasifier, the Free Fall Swelling Test seemed to be the better choice to study thermoplasticity at CCG conditions.

Effect of Pressure

Thermoplastic behavior of potassium-catalyzed Illinois No. 6 coal was first observed in CCG work during large scale char preparation in a 0.78 MPa/3 $kg\text{-}ks^{-1}$ Fluid Bed Gasifier (FBG). Fluid bed densities which were lower than previously measured were noted in the FBG[3]. During start-up of the PDU with the same coal, feedline plugging caused by agglomeration was frequently a problem[4]. Fixed bed laboratory tests then identified pressure as one important variable in catalyzed coal agglomeration[5]. PDU runs also suggested the importance of pressure, and of oxidation, to fluid bed density[1b]. However, since other variables such as superficial velocity changed along with pressure, it was difficult to uniquely determine the effect of pressure on thermoplasticity and gasifier properties.

The variation of the loose bulk density of pyrolyzed coal from the Free Fall Swelling Test with pressure (Figure 3) is in agreement with this earlier data which indicate that higher pressures increase coal thermoplasticity. The densities of uncatalyzed and catalyzed-oxidized Illinois No. 6 coals decrease as the Free Fall Unit pressure is raised above atmospheric pressure. Char densities at 3.5 MPa fall into the expected order: catalyzed-oxidized > catalyzed > uncatalyzed. The reproducibility of the measurement is indicated by good agreement between the two sets of data on catalyzed-oxidized coal (Figure 3, □ and △). The effect of pressure on thermoplasticity, as manifested by swelling, was later directly observed by fast photography of single particles of potassium catalyzed Illinois No. 6 coal (FILM SEGMENT #2: Illinois + 12.2 wt % KOH at 3.5 MPa). These films show more swelling at 3.5 MPa than at 0.1 MPa.

This trend is attributed to the effect of pressure on the volatile components during the extremely rapid pyrolysis. It is thought that higher pressure retards the escape of volatile pyrolyzates from coal particles by shifting the boiling points of the volatile components to a higher temperature range. Because of the short time involved with the rapid heating, most of the volatile components will remain in the particle until they begin to boil (i.e., their vapor pressure equals the total pressure of the system). With the more volatile and, hence, likely less viscous and solvent-like components retained to a higher temperature, the coal attains a lower viscosity during the plastic transition. Because of this lower viscosity, the evolving gas has a greater swelling effect on the unconstrained, free falling, plastic coal particle. At a pressure of approximately 1.5 MPa (200 psig), the majority of the components that will affect the viscosity of the particle appear to have been retained, for further increase of pressure has little effect on swelling (loose bulk density). Increased pressure is expected to reduce the total volume of pyrolysis gases released, but because the gas volume is still many times greater than the volume of the resulting char, increasing pressure from 1.5 to 5.5 MPa (200 to 800 psig, or decreasing the volume of the pyrolysis gases by a factor of four) should not have a large effect on swelling. If this line of thinking is extended, it would predict that swelling will begin to decrease at much higher pressures where the volume of the evolving gases is contracted severely (loose bulk density will increase).

Effect of Catalyst, Oxidation and Longer Particle Penetration Time

The effects of catalyst, oxidation, and longer penetration time on thermoplasticity, as measured by FFSI, are summarized for several coals of interest to CCG in Figures 4-7. These include Illinois No. 6, Valley Camp, and Hawk's Nest coals which are bituminous in rank, and Wyodak coal which is sub-bituminous in rank.

The effect of potassium catalyst is to reduce thermoplasticity whether the coal is purposely oxidized prior to catalyst addition or not (Figure 4). The exception is Wyodak coal which is very close to being non-swelling even without potassium catalyst. Decreased swelling upon catalyst addition is thought to be due to the factors of salt formation between the catalyst and the coal, and reduced pyrolysis.

Oxidation after catalyst addition reduces swelling for the more porous Illinois No. 6 (13 wt % equilibrium moisture, uncatalyzed) but does little for the much less porous Hawk's Nest coal (5 wt % equilibrium moisture, uncatalyzed; Figure 5). This suggests that oxygen has difficulty penetrating less porous particles.

Mild oxidation alone can reduce swelling without catalyst addition, and more extensive oxidation reduces swelling still further. However, the application of potassium catalyst after oxidation results in a large additional reduction of swelling, presumably because the aqueous application allows the catalyst to migrate to new surface acids formed during oxidation. This is demonstrated by lower FFSI's after additional penetration time is allowed the catalyst. The effect of poor catalyst dispersion is also discussed in the next section.

The sequence of increasing coal swelling after catalyst application and oxidation in preparation for PDU operation is, as shown in Figure 7, Wyodak (FFSI=1.0) < Illinois (FFSI=2.5-2.85) < Valley camp (FFSI=3.1) < Hawk's Nest (FFSI=3.6-4.5).

Effect of Catalyst Dispersion

Even when mixed with potassium catalyst in an aqueous slurry and given an extended soak at mild conditions, some coals such as Hawk's Nest coal do not take up the catalyst effectively. The catalyst lays down as a rim on the exterior of particles which can clearly be seen in Scanning Electron Microscope (SEM) photomicrographs of particle cross-sections. When heated in the fast photography cell, these particles exhibit two distinct thermal behaviors. The well-catalyzed outer rim does not melt on heating, but merely cracks. The poorly catalyzed particle interior does melt and flows out through the cracks in the unmelted outer rim (FILM SEGMENT #3: Hawk's Nest + 12.2 wt % KOH).

Effect of Atmosphere

The effect of selected inert and reactive gases on residue loose bulk density was examined because there are a variety of gases in a CCG atmosphere which may have different effects on thermoplasticity. Other work has shown that the nature of the gas atmosphere does affect thermoplasticity at pressure as measured by maximum fluidity in a plastometer[6]. In the Free Fall Swelling Test, it was found that H_2, He, CO_2, Ar, and N_2 gave residues with densities which spanned a range of only 0.02 g/cc (Figure 8). The cause of this small difference is thought to be the speed with which pyrolysis takes place in the Free Fall Swelling Test. Under conditions of rapid pyrolysis, it may be possible for particles to become blanketed in an atmosphere of their own pyrolyzates which isolates the particles from the bulk atmosphere. If some additional conversion does occur in reactive gases (H_2, CO_2), then densification must occur at the same time in order for the coke densities to be so similar.

Summary

We have found the Free Fall Swelling Test to be helpful in the guidance of pilot plant work and in determining the effect of several CCG variables on thermoplasticity. Under the test conditions of high pressure and high heat-up rate, the coal thermoplastic property is more pronounced than at conditions of low heat-up rate and low pressure under which more conventional tests for thermoplasticity are run. Thus, the test is a more sensitive probe of the thermoplastic tendency, especially for coals having a limited thermoplastic tendency.

References

1. (a) T. Kalina and N. C. Nahas, "Exxon Catalytic Coal Gasification Process Predevelopment Program", Final Project Report for the U. S. Department of Energy under Contract No. E(49-18)-2369, December, 1978.

   (b) C. A. Euker and R. A. Reitz, "Exxon Catalytic Coal Gasification Process Development Program", Final Project Report for the U. S. Department of Energy under Contract No. ET-78-C-01-2777, November, 1981.

   (c) R. A. Cardello, R. A. Reitz and F. C. R. M. Smits, "Catalytic Coal Gasification Development", presented in Round Table Discussion No. 5, 11th World Petroleum Congress, London, England, August, 1983.

2. (a) D. W. Van Krevelen, "Coal: Typology - Chemistry - Physics - Constitution", Elsevier, New York, 1961.

   (b) D. Habermehl, F. Orywal and H. Beyer, "Chemistry of Coal Utilization", ed. M. A. Elliot, Wiley, New York, 1981, 317-368.

   (c) M. S. Lancet, F. A. Sim and G.P. Curran, Prepr., Am. Chem. Soc., Div. Fuel Chem., 27 (1), 1-24 (1982); EPRI Final Report, AP-2335 (April, 1982).

References (continued)

(d) R. J. Tyler, FUEL, 58(9), 680-686 (1979).

(e) M. S. Lancet and F. A. Sim, Prepr., Am. Chem. Soc., Div. Fuel Chem., 26(3), 167-171 (1981).

(f) R. Loison, A. Peytavy, A. F. Boyer and R. Grillot, "Chemistry of Coal Utilization," ed. H. H. Lowry, Wiley, New York, 1963, 150-201.

(g) M. R. Khan and R. G. Jenkins, FUEL, 63(1), 109-115 (1984); EPRI, Final Report, AP-2337 (April, 1982).

(h) P. Arendt, M. Kaiser, W. Wanzl and K. H. van Heek, in "Proceedings, International Conference on Coal Science", Verlag Gluckauf Gmbh, Essen, 1981, 618-623.

3. C. A. Euker, "Exxon Catalytic Coal Gasification Process Develoment Program", Monthly Technical Progress Report for the U. S. Department of Energy under Contract No. ET-78-C-01-2777, November, 1978.

4. C. A. Euker, "Exxon Catalytic Coal Gasification Process Development Program", Monthly Technical Progress Report for the U.S. Department of Energy under Contract No. ET-78-C-01-2777, July, 1979.

5. C. A. Euker, "Exxon Catalytic Coal Gasification Process Development Program", Monthly Technical Progress Report for the U.S. Department of Energy under Contract No. ET-78-C-01-2777, January, 1980.

6. M. Kaiho and Y. Toda, FUEL, 55, 397-398 (1979).

TABLE 1

CHARACTERISTICS OF PDU FEED COALS (UNCATALYZED)

	Illinois No. 6 (Monterey No. 1)	Hawk's Nest	Valley Camp	Walden	Wyodak
Coal Rank	Bituminous	Bituminous	Bituminous	Bituminous	Sub-bituminous
Equilibrium Moisture (Wt %)	13.4	5.1	7.4	9.5	28.7
Free Swelling Index	4	3	2	0.5	0
Ultimate Analysis (Wt % Dry Coal)					
Carbon	69.4	75.6	73.3	69.6	67.0
Hydrogen	4.8	5.4	5.6	4.8	5.2
Oxygen (Difference)	8.9	10.2	11.7	12.6	15.3
Nitrogen	1.4	1.7	1.4	1.3	1.0
Sulfur, Total	4.6	0.5	0.7	0.6	1.0
Pyritic	0.8	0.1	0.2	0.3	0.2
Sulfate	0.1	0.0	0.0	0.0	0.2
Organic	3.8	0.4	0.5	0.3	0.7
Chlorine	0.2	0.1	0.0	0.0	0.0
Ash Elements (SO_3-Free, % Ash, Dry)					
SiO_2	51.0	51.1	60.0	54.5	40.6
Al_2O_3	18.4	23.9	11.3	29.0	22.7
P_2O_5	0.4	0.9	0.3	1.0	1.2
TiO_2	1.1	1.1	1.0	0.7	1.7
Fe_2O_3	19.8	10.7	7.4	5.0	6.0
CaO	4.9	7.8	16.2	8.0	21.2
MgO	1.0	2.0	2.4	0.8	5.2
K_2O	2.1	1.4	1.2	0.3	0.5
Na_2O	1.4	1.1	0.3	0.8	0.9

Table 2

ASTM Free Swelling Index (FSI) and Free Fall Swelling Index (FFSI) of Selected CCG Coals

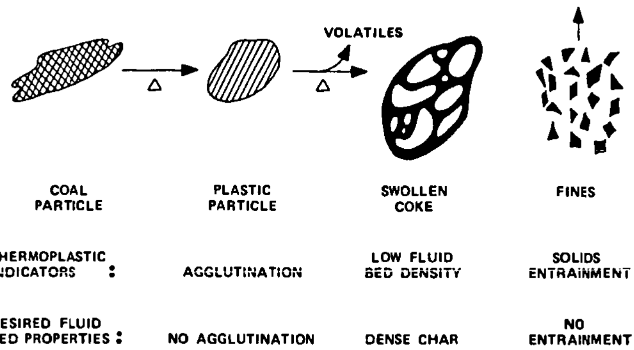
Coal	ASTM FSI	FFSI[a]	Free Fall Residue Density, g/cc
A Wyodak + K	0.0 (no swelling)	1.0	0.37
B Illinois No. 6 + K (oxid.)	0.0 (no swelling)	2.6	0.15
C Illinois No. 6 + K (unox.)	0.5 (no swelling)	5.6	0.09

(a) FFSI conditions were 978°K and 3.5 MPa.

84B-3-152

FIGURE 1

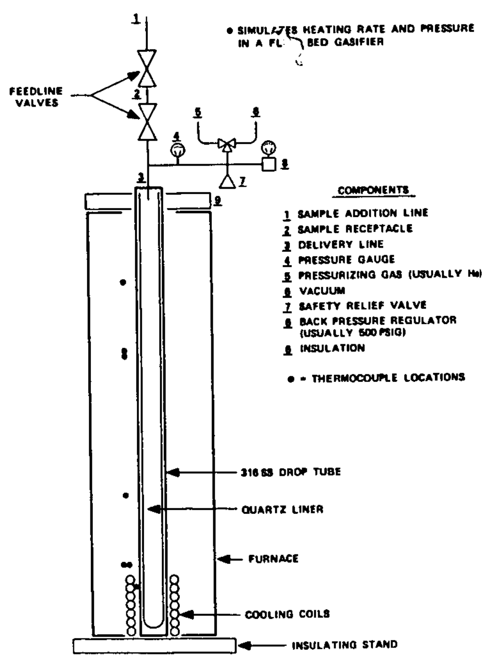
SOME CATALYZEO BITUMINOUS COALS EXHIBIT UNDESIRABLE THERMOPLASTIC BEHAVIOR WHEN FED TO A FLUID BEO GASIFIER



84B-3-154

FIGURE 2

FREE FALL UNIT SCHEMATIC

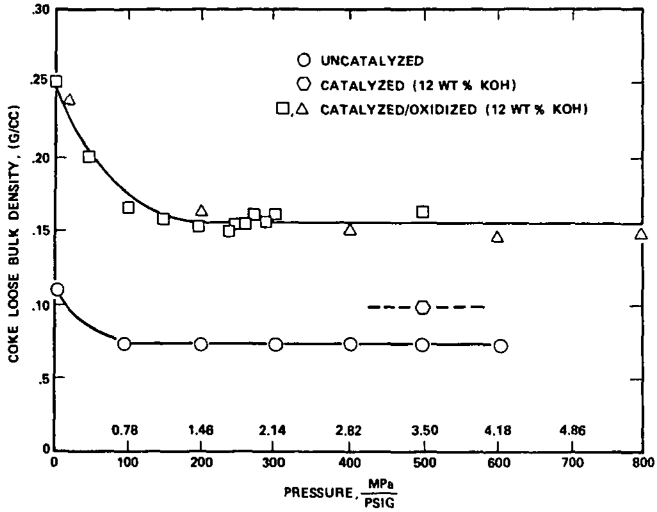


84B-3-155

FIGURE 3

INCREASED PRESSURE DECREASES ILLINOIS CHAR DENSITY

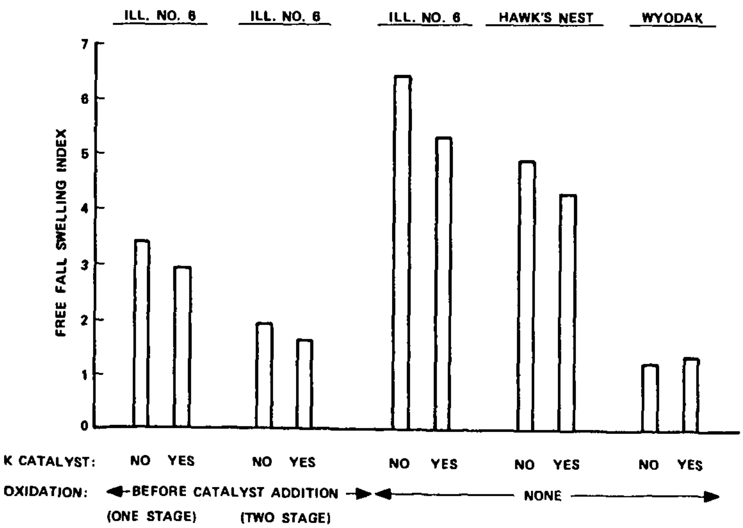
- HELIUM ATMOSPHERE
- 1033°K
- ILLINOIS NO. 6 COAL



84B-3-176

FIGURE 4

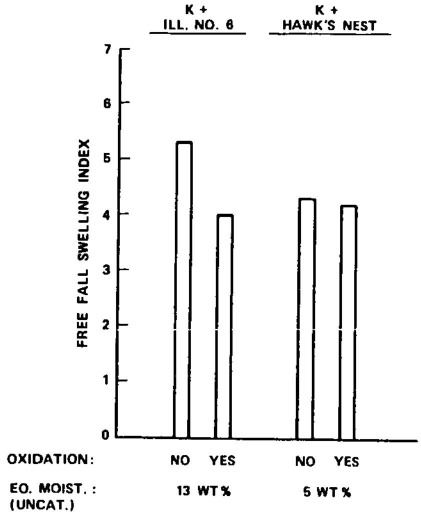
CATALYST REDUCES THERMOPLASTIC SWELLING



84B-3-177

FIGURE 5

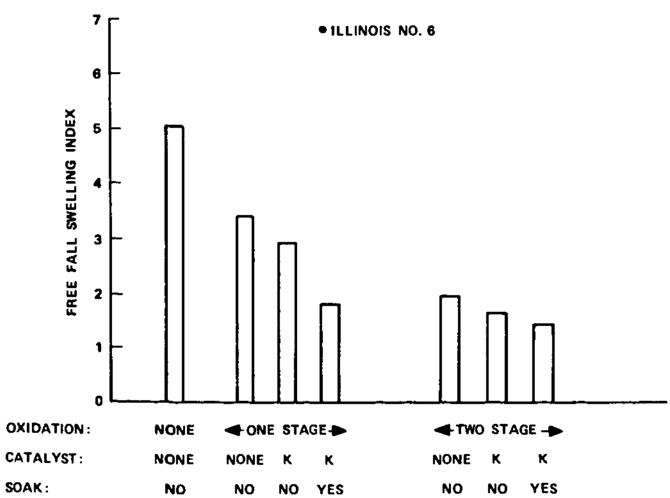
OXIDATION REDUCES SWELLING OF THE MORE POROUS COAL



84B-3-178

FIGURE 6

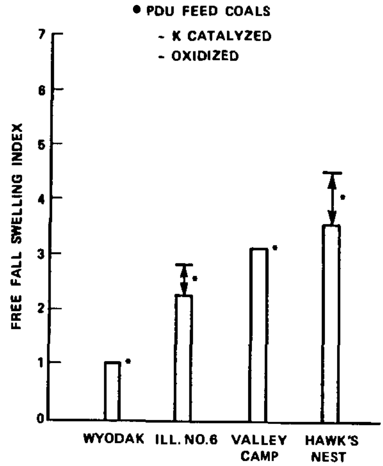
WHILE OXIDATION ALONE HAS AN EFFECT, CATALYST APPLICATION AND INCREASED PARTICLE PENETRATION TIME RESULT IN AN ADDITIONAL REDUCTION OF SWELLING



84B-3-179

FIGURE 7

THERMOPLASTIC SWELLING OF CCG COALS VARIES



* RANGE OF VALUES

84B-3-157

FIGURE 8

ATMOSPHERIC EFFECTS ON RESIDUE LOOSE BULK DENSITY ARE SMALL AT HIGH PRESSURE